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Structure of [1*S*-(1α,4aα,7β,7aα)]-1-β-D-Glucopyranosyloxy-1,4a,5,6,7,7a-hexahydro-7-methylcyclopenta[*c*]pyran-4-carbaldehyde (Boschnaloside) Monohydrate*

By M. Soriano-García,† R. A. Toscano, M. Jiménez and A. Lira-Rocha

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, *Mexico DF*

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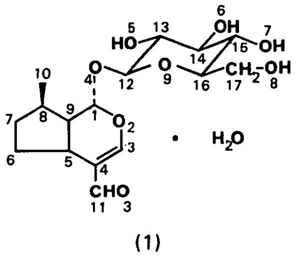
Abstract. $C_{16}H_{24}O_8.H_2O$, $M_r = 362{\cdot}4$, monoclinic, $P2_1$, $a = 8{\cdot}090\,(3)$, $b = 7{\cdot}739\,(2)$, $c = 14{\cdot}416\,(5)$ Å, $\beta = 102{\cdot}26\,(3)°$, $V = 882\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}36$ Mg m^{-3}, $\lambda(\text{Cu }K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}841$ mm^{-1}, $F(000) = 388$, $T = 293$ K, final $R = 0{\cdot}060$ for 1259 observed reflections. The structure deduced by chemical and spectroscopic methods is confirmed. The title compound, boschnaloside, is an iridoid glucoside. The five-membered and dihydropyran rings adopt envelope and sofa conformations, respectively. The β-glucose moiety adopts a $^4C_1$ chair conformation. There are no unusual bond distances or angles. The crystal structure is stabilized by a three-dimensional network of O—H···O and C—H···O hydrogen bonds.

Introduction. The naturally occurring iridoid glucoside (boschnaloside) (1) was isolated from aerial parts of the plant *Penstemon rosseus* (Schrophulariaceae). This plant is widely distributed in Mexico. A chemical structure of (1) was assigned by Sakan, Murai, Hayashi, Honda, Shono, Nakajima & Kato (1967) and Murai & Tagawa (1980) from spectral (IR, UV and NMR) and chemical methods.

The X-ray crystallographic structure determination of (1) was undertaken in order to ascertain its conformation and molecular geometry.



(1)

Experimental. Colourless crystal 0·05 × 0·40 × 0·44 mm. Nicolet *R*3 four-circle diffractometer, graphite-monochromated Cu $K\alpha$; lattice parameters from 15 machine-centred reflections with $6{\cdot}3 < 2\theta < 26{\cdot}7°$; 1408 reflections with $3 < 2\theta < 115°$ for two octants, 1259 independent with $I > 2{\cdot}5\sigma(I)$, $R_{\text{int}} = 0{\cdot}03$; index range h ±8, k 0→7, l 0→15; ω-scan mode, variable scan speed, scan width 1·0° (θ); two standard reflections (200, 112) monitored every 50 measurements; Lp correction, absorption ignored; structure solved by direct methods using *SHELXTL* (Sheldrick, 1981); least-squares refinement of all non-H atoms treated anisotropically; atoms C(7) and C(10) show some disorder (see thermal parameters in Table 1); H atoms riding on the bonded C with fixed isotropic temperature factor, $U = 0{\cdot}06$ Å^2; H atoms bonded to O refined; $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + 0{\cdot}005(F_o)^2]^{-1}$: in the last cycle $(\Delta/\sigma)_{\max} = 0{\cdot}44$; residual electron density between −0·26 and 0·41 e Å^{-3}; isotropic-extinction parameter $X = 0{\cdot}035$; final $R = 0{\cdot}060$, $wR = 0{\cdot}095$, $S = 1{\cdot}35$; scattering factors from *International Tables for X-ray Crystallography* (1974); all computations performed on a Nova 4S computer and plots on a Tektronix plotter with the *SHELXTL* system of programs (Sheldrick, 1981).

Discussion. Atomic coordinates are in Table 1.‡ A perspective molecular drawing, the atomic labelling and selected torsion angles are displayed in Fig. 1. Bond distances and angles are listed in Table 2.

The absolute configuration of (1) was not determined directly, but was inferred from the known configuration of the glucose moiety and from chemical and spectroscopic studies (Murai & Tagawa, 1980).

The five-membered ring C(5)—C(9) occurs in an envelope conformation with C(5) as the flap −0·31 (1) Å out of the best plane formed by the other four ring atoms. The fusion to the dihydropyran ring is *cis* with torsion angles in the five- and six-membered rings about the common bond of 18·5 (5) and 27·4 (6)°, respectively (see Fig. 1).

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* Contribution No. 790 of the Instituto de Química, UNAM.

† To whom correspondence should be addressed.

‡ Lists of structure amplitudes, anisotropic thermal parameters, the results of mean-plane calculations, H-atom coordinates and H-bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42835 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The dihydropyran ring adopts a sofa conformation with C(1) as the flap −0·60 (1) Å out of the plane of the other atoms. The ring torsion angles differ from those of the ideal sofa [0, 0, 28, −56, 54, −27° cyclically, starting from the double bond (Bucourt & Hainaut, 1965)] by an average of 3°. This type of conformation has been observed in loganin (Jones, Sheldrick, Glüsenkamp & Tietze, 1980).

The β-glucose moiety adopts the $^4C_1$ conformation as in most D-pyranoses (Ohanessian, Longchambon & Arene, 1978). The values of the ring torsion angles are in agreement with the values found in the β-glucopyranose residue of β-maltose monohydrate (Gress & Jeffrey, 1977) and in decentapicrin A (Kojić-Prodić, Spek, van der Sluis & Labadie, 1985). The conformation around the glycosidic bond is defined

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² × 10³) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{\rm eq}$
O(2)	5336 (4)	13834	2285 (2)	52 (1)
O(3)	11229 (5)	13221 (10)	2867 (6)	122 (3)
O(4)	5567 (4)	10977 (5)	2810 (2)	47 (1)
O(5)	6580 (4)	9766 (6)	1163 (2)	56 (1)
O(6)	4989 (4)	6750 (5)	412 (2)	58 (1)
O(7)	1349 (4)	6605 (5)	455 (3)	56 (1)
O(8)	−382 (5)	9503 (6)	2518 (3)	65 (2)
O(9)	3101 (4)	9477 (5)	2432 (2)	47 (1)
O(1)	8172 (5)	8129 (6)	9664 (3)	61 (1)
C(1)	5238 (6)	12710 (7)	3055 (4)	47 (2)
C(3)	6926 (7)	14003 (7)	2121 (4)	55 (2)
C(4)	8329 (6)	13661 (7)	2764 (4)	50 (2)
C(5)	8349 (5)	13180 (7)	3764 (3)	55 (2)
C(6)	9249 (8)	14549 (10)	4471 (5)	83 (2)
C(7)	7928 (11)	15441 (20)	4708 (15)	365 (11
C(8)	6274 (8)	14828 (8)	4481 (4)	69 (2)
C(9)	6537 (6)	13123 (7)	3948 (3)	50 (1)
C(10)	5064 (18)	16068 (15)	3971 (6)	197 (6)
C(11)	9896 (7)	13683 (7)	2399 (6)	79 (2)
C(12)	4412 (5)	10298 (7)	2060 (3)	44 (1)
C(13)	5318 (5)	8955 (6)	1580 (3)	42 (1)
C(14)	4070 (5)	8027 (7)	807 (3)	45 (1)
C(15)	2626 (5)	7270 (6)	1218 (3)	41 (1)
C(16)	1848 (5)	8696 (6)	1694 (3)	42 (1)
C(17)	473 (6)	8091 (7)	2202 (4)	52 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(2)—C(1)	1·426 (6)	O(2)—C(3)	1·362 (7)
O(3)—C(11)	1·199 (8)	O(4)—C(1)	1·426 (7)
O(4)—C(12)	1·375 (5)	O(5)—C(13)	1·435 (6)
O(6)—C(14)	1·426 (6)	O(7)—C(15)	1·436 (5)
O(8)—C(17)	1·420 (7)	O(9)—C(12)	1·435 (6)
O(9)—C(16)	1·437 (5)	C(1)—C(9)	1·512 (6)
C(3)—C(4)	1·331 (7)	C(4)—C(5)	1·486 (8)
C(4)—C(11)	1·472 (9)	C(5)—C(6)	1·542 (9)
C(5)—C(9)	1·544 (7)	C(6)—C(7)	1·376 (16)
C(7)—C(8)	1·391 (12)	C(8)—C(9)	1·565 (8)
C(8)—C(10)	1·454 (13)	C(12)—C(13)	1·520 (7)
C(13)—C(14)	1·516 (6)	C(14)—C(15)	1·534 (7)
C(15)—C(16)	1·506 (7)	C(16)—C(17)	1·529 (7)
C(1)—O(2)—C(3)	113·8 (3)	C(1)—O(4)—C(12)	115·0 (3)
C(12)—O(9)—C(16)	111·7 (3)	O(2)—C(1)—O(4)	109·7 (4)
O(2)—C(1)—C(9)	113·0 (4)	O(4)—C(1)—C(9)	106·1 (4)
O(2)—C(3)—C(4)	123·9 (5)	C(3)—C(4)—C(5)	123·8 (5)
C(3)—C(4)—C(11)	114·9 (5)	C(5)—C(4)—C(11)	121·1 (5)
C(4)—C(5)—C(6)	112·1 (5)	C(4)—C(5)—C(9)	111·0 (4)
C(6)—C(5)—C(9)	103·8 (4)	C(5)—C(6)—C(7)	103·1 (7)
C(6)—C(7)—C(8)	122·0 (13)	C(7)—C(8)—C(9)	100·3 (8)
C(7)—C(8)—C(10)	113·8 (10)	C(9)—C(8)—C(10)	117·1 (5)
C(1)—C(9)—C(5)	111·9 (4)	C(1)—C(9)—C(8)	117·0 (4)
C(5)—C(9)—C(8)	107·1 (4)	O(3)—C(11)—C(4)	122·4 (8)
O(4)—C(12)—O(9)	107·9 (3)	O(4)—C(12)—C(13)	107·9 (3)
O(9)—C(12)—C(13)	109·5 (4)	O(5)—C(13)—C(12)	110·3 (4)
O(5)—C(13)—C(14)	108·8 (4)	C(12)—C(13)—C(14)	110·4 (3)
O(6)—C(14)—C(13)	107·5 (3)	O(6)—C(14)—C(15)	113·2 (4)
C(13)—C(14)—C(15)	109·8 (4)	O(7)—C(15)—C(14)	108·9 (4)
O(7)—C(15)—C(16)	108·0 (3)	C(14)—C(15)—C(16)	108·8 (4)
O(9)—C(16)—C(15)	110·4 (3)	O(9)—C(16)—C(17)	104·1 (4)
C(15)—C(16)—C(17)	114·3 (4)	O(8)—C(17)—C(16)	111·9 (4)

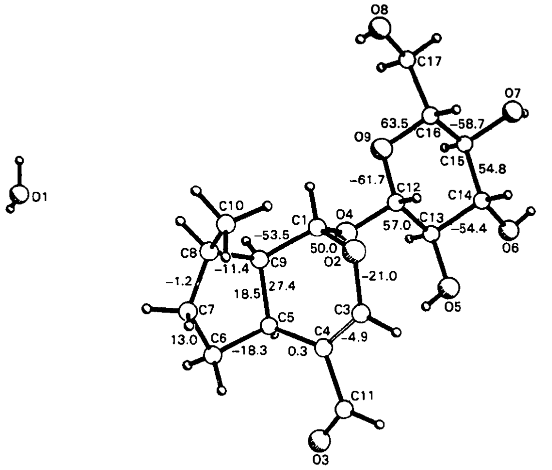

Fig. 1. View of the molecule of boschnaloside, showing the atom labelling and selected torsion angles; e.s.d.'s are 0·5–0·8°, apart from those involving C(7) which are 1·0–1·8°.

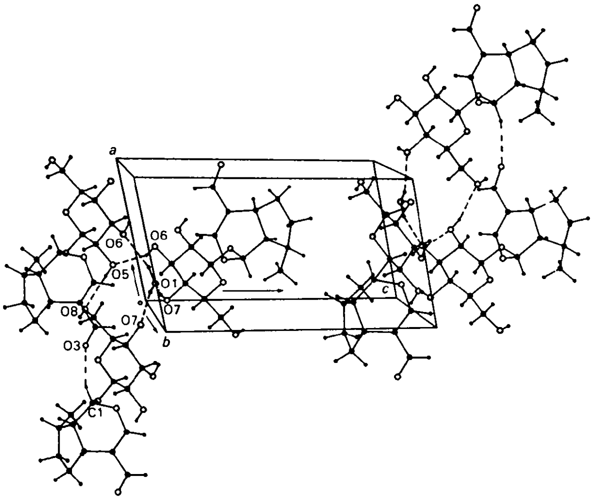

Fig. 2. A perspective drawing of the packing arrangement. The dashed lines indicate the intermolecular hydrogen bonds.

by the torsion angle 174·2 (4)° for the atom sequence C(12)—O(4)—C(1)—C(9).

The extensive system of hydrogen bonds in the crystal structure of (1) is illustrated in Fig. 2.* There are no intramolecular hydrogen bonds and neither the glycosidic bridge O nor the ring O atoms are hydrogen-bonded. Two hydroxyl groups in the molecule exhibit both donor and acceptor functions. Each molecule is linked to a neighbour by O(5)—H(5A)···O(8); C(1)—H(1)···O(3)($-1 + x, y, z$) to form chains parallel to **a**. The water molecule is involved in three hydrogen bonds [O(1)—H(1B)···O(6)($x, y, 1+z$), O(1)—H(1A)···O(7) ($1 + x, y, 1 + z$) and O(7)—H(7)···O(1)($1 - x, -0{\cdot}5 + y, 1 - z$)] with three neighbouring molecules.

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* See deposition footnote.

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cis-Thymidine 3′,5′-Cyclic Methylphosphonate Acetone Solvate, a Cyclic Nucleotide with an Axial Methyl Group on Phosphorus

BY WESLEY G. BENTRUDE,* ALAN E. SOPCHIK, GURDIP S. BAJWA AND WILLIAM N. SETZER

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112, *USA*

AND WILLIAM S. SHELDRICK*†

Gesellschaft für Biotechnologische Forschung MbH, Mascheroder Weg 1, *D*-3300 *Braunschweig-Stöckheim, Federal Republic of Germany*

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Abstract. $C_{11}H_{15}N_2O_6P.C_3H_6O$, $M_r = 360{\cdot}30$, monoclinic, $C2$, $a = 18{\cdot}298\ (6)$, $b = 7{\cdot}251\ (2)$, $c = 13{\cdot}618\ (2)$ Å, $\beta = 96{\cdot}41\ (3)°$, $V = 1795{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 16{\cdot}82$ cm^{-1}, $F(000) = 760$, $T = 293$ K, $R = 0{\cdot}039$ for 1622 unique observed reflections. The compound crystallizes with one cyclic nucleotide molecule and one acetone solvent molecule in the asymmetric unit. The conformation of the thymine base is *anti*. The ribose ring adopts a T_4^3 [C(4′)-*exo*/C(3)′-*endo*] (half-chair) conformation, and the phosphonate ring adopts a flattened-chair conformation with the methyl group axial.

Introduction. We have been interested in the conformational consequences of phosphorus substituents in 3′,5′-cyclic nucleotides. Recently we have studied, using NMR (Nelson, Sopchik & Bentrude, 1983; Bajwa & Bentrude, 1978, 1980; Sopchik, Bajwa, Nelson & Bentrude, 1981; Sopchik & Bentrude, 1980) and X-ray diffraction (Bentrude, Sopchik, Setzer, Bates & Ortega, 1986; Newton, Pantaleo, Bajwa & Bentrude, 1977), the conformational properties of neutral derivatives of nucleoside 3′,5′-cyclic monophosphates. This paper reports the crystal structure of *cis*-thymidine 3′,5′-cyclic methylphosphonate, (1), a cyclic nucleotide

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* Address correspondence to these authors.

† Current address: Universität Kaiserslautern, Postfach 3049, D-6750 Kaiserslautern, Federal Republic of Germany.

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